

RESEARCH PAPER

Comparison of commercial glyphosate formulations for control of prickly sida, purple nutsedge, morningglory and sicklepod

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The efficacy of the commercial glyphosate [(N-phosphonomethyl) glycine] formulations Roundup Ultra, Touchdown and Engame were compared for the control of prickly sida (*Sida spinosa* L.), morningglory (*Ipomeae hederacea* var. *integriscula* Gray), sicklepod (*Senna obtusifolia* L.) and purple nutsedge (*Cyperus rotundus* L.). Engame is a new formulation of glyphosate that contains glyphosate acid and 1-aminomethanamide dihydrogen tetraoxosulfate (AMADS), a proprietary mixture of sulfuric acid and urea, other than glyphosate salt and surfactants. Injury by Engame differed from Roundup Ultra and Touchdown in that necrotic lesions formed on leaves several hours after treatment. Leaves of very susceptible species, such as prickly sida, were rapidly, although incompletely, desiccated and then became chlorotic and died in a manner typical of other glyphosate formulations. Engame was 2–3 times more active to growth inhibition than either the Roundup Ultra or Touchdown formulations, based on GR₅₀ comparisons expressed on an acid equivalent basis. The GR₅₀ estimates did not change over the 3 week evaluation period for prickly sida and purple nutsedge, and after 2 weeks after treatment for morningglory. The GR₅₀ estimates for sicklepod decreased over the 3 week evaluation period indicating a slower response to glyphosate. The application of AMADS alone caused minute necrotic lesions on sicklepod and purple nutsedge, and lesions up to 3 mm in diameter on prickly sida and morningglory. Further injury from AMADS was not noted and plants resumed growth without apparent delay. At glyphosate rates above 1120 g ha⁻¹, greater than 80% control was achieved at 7 days after treatment. These results demonstrate that glyphosate efficacy can be further enhanced by formulations that apparently improve uptake and translocation.

Keywords: efficacy, formulation, glyphosate.

INTRODUCTION

The effects of formulation and additives on glyphosate efficacy have been studied for over 30 years and several reviews have been published (Turner 1985; Franz *et al.* 1997). Commercial glyphosate formulations usually

contain a monovalent salt of glyphosate because these salts have water solubilities that may exceed 50% (Baird *et al.* 1971; Franz *et al.* 1997). The high water solubility of glyphosate salts allows manufacturers to achieve the loading capacity desired in commercial concentrates. Surfactants are usually included because they almost always improve the efficacy and rainfastness of glyphosate salts (Coble & Brumbaugh 1993; De Ruiter *et al.* 1996; Franz *et al.* 1997). For example, Roundup Ultra contains the isopropylamine salt of glyphosate and a modified tallowamine surfactant and Touchdown contains the trimesium salt of glyphosate and an alkyl polyglucoside surfactant. Each formulation contains 480 g ai L⁻¹. Glyphosate also forms divalent and trivalent salts with metal cations, such as calcium, zinc and iron;

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however, these have low water solubilities (Franz *et al.* 1997) rendering them unsuitable for formulation. Similarly, glyphosate acid, while toxic (Laerka & Streibig 1995; Nalewaja *et al.* 1996), has a relatively low water solubility of 1.2% at 25°C (Baird *et al.* 1971), compared with the monovalent salts, making it less suitable for commercial concentrates.

Adjuvants, particularly ammonium sulfate, have been shown to enhance glyphosate activity (Suwunnamek & Parker 1975; Wills & McWhorter 1985; De Ruiter *et al.* 1996). Enhancement in some cases may be substantial, as in the control of quackgrass, where ammonium sulfate at 7.5 g L⁻¹ decreased the ED₅₀ for glyphosate fivefold (De Ruiter *et al.* 1996). However, enhanced control or activity by addition of ammonium sulfate is not always realized (Nalewaja & Matysiak 1992; Jordan *et al.* 1997). The enhancement effect by ammonium sulfate was thought to be due to diminished glyphosate antagonism resulting from complexation with metal cations contained in the water used (Nalewaja & Matysiak 1993). Divalent and trivalent acids, such as sulfuric and orthophosphoric acids, also enhanced glyphosate activity and prevented antagonism of glyphosate efficacy by calcium chloride or sodium hydrogen carbonate (Nalewaja & Matysiak 1993). However, Thelen *et al.* (1995) indicated that ammonium sulfate per se has no metal binding property so its effect can be due to inhibition of metal complexation with glyphosate. In these cases, the effect may have been due to the low solubility of calcium or metal salts in these acids. Other salts (Wills & McWhorter 1985) and urea (Suwunnamek & Parker 1975) also enhanced the efficacy of glyphosate.

Engame (Engame Technical Bulletin 2001) is a new formulation of glyphosate consisting of glyphosate acid (152 g L⁻¹ or 9.6%) and 1-aminomethanamide dihydrogen tetraoxosulfate (AMADS) (1091 g L⁻¹ or 71.1%). AMADS (Entek Corporation, Elkridge, MD, USA) is a proprietary mixture of sulfuric acid and urea that acts as a synergist for glyphosate acid (Engame Technical Label). As previously noted, urea and sulfuric acid have been shown to enhance glyphosate activity individually. Engame was reported to be more active than other formulations of glyphosate (Molin 2000; Parrish 2002; Westra *et al.* 2002).

Engame, upon dilution for application, produces a solution with a pH < 2.0. The value of the first dissociation constant of glyphosate is $pK_{a1} = 2.27$ (Franz 1985) so at pH < 2, glyphosate would be mostly protonated and would not readily bind divalent cations. Thus, AMADS may reduce glyphosate binding with divalent cations,

similar to sulfuric acid and ammonium sulfate in solution, and allow more glyphosate uptake without antagonism from calcium or other salts. In addition, the low pH of Engame solutions can injure or kill cells beneath the cuticle (Molin *et al.* 2003), which may further increase glyphosate acid uptake. Recently, Westra *et al.* (2003) reported that Engame was twice as active as Roundup Ultra at equivalent rates of glyphosate. They also found that twice as much Engame was absorbed compared to Roundup Ultra using radiolabeled glyphosate. The mechanism of enhanced uptake was not determined.

The objectives of the present study are to describe the effects and compare the efficacy of glyphosate formulated in Engame, Roundup Ultra and Touchdown by the GR₅₀ concentration for each formulation against weeds with high, moderate and low tolerance to glyphosate.

MATERIALS AND METHODS

Prickly sida, sicklepod and morningglory were established from seed and purple nutsedge from two-leaf stage seedlings. Seeds or two-leaf stage purple nutsedge seedlings were placed in 10 cm diameter pots containing a 4 : 1 (w : w) mixture of soil (Dundee silty clay loam, fine-silty, mixed thermic Aeric Ochraqualf) and Jiffy Mix (Jiffy Products of America, Batavia, IL, USA). Pots were placed in the greenhouse at 30 ± 2°C and a photoperiod of 14 h. Pots were subirrigated as needed and fertilized biweekly with 50 mL of 1% (w : v) General Purpose Water Soluble Fertilizer (Scotts-Sierra Horticultural Products Corp., Marysville, OH, USA). Prickly sida and purple nutsedge were sprayed at the four-leaf stage, and sicklepod and morningglory at the two-leaf stage.

Herbicides were applied with a pneumatic track sprayer (Allen Machine Works, Midland, MI, USA) with Teejet 8002 flat fan spray tips delivering 187 L ha⁻¹ water at 179 kPa. Touchdown and Roundup Ultra were applied without additional surfactant. Engame was applied in solution containing 0.1% Breakthru surfactant (Goldschmidt Chemical Corp., Hopewell, VA, USA). Glyphosate was applied at 11, 22, 56, 112, 224, 560, 1120 and 2240 g ae ha⁻¹. AMADS was also tested for its capacity to injure these weeds at the rates present in Engame.

A randomized complete block design with four replications was used and the experiment was repeated. The data were not significantly different in each experiment and the data were combined. Plants were evaluated for injury expressed as growth reduction relative to

untreated plants (control) at 1, 2 and 3 weeks after treatment (WAT) and the data were recorded as injury as a percentage of the control, where 0% of the control was complete kill and 100% no injury. The GR_{50} , the concentration of the acid equivalent of glyphosate to cause 50% growth reduction, and the asymptotic standard error and 95% confidence intervals were calculated using the dose-response model of Seefeldt *et al.* (1995) using SAS (SAS 2002). In this model, the data are fitted to the dose-response model $y = C + (D - C) / 1 + \exp[b(\log(x - \log(GR_{50})))]$, where response y is related to dose x , D is the mean response of the control, C the mean response at very high doses, and b the slope of the curve around the GR_{50} .

RESULTS AND DISCUSSION

Figures 1–4 show the dose-response curves for the effects of Engame, Roundup Ultra and Touchdown formulations of glyphosate on the injury to prickly sida, purple nutsedge, morningglory and sicklepod at 3 WAT. In each case, the Engame formulation was more active than either Roundup Ultra or Touchdown. The responses of prickly sida, sicklepod and purple nutsedge to Roundup Ultra and Touchdown were very similar

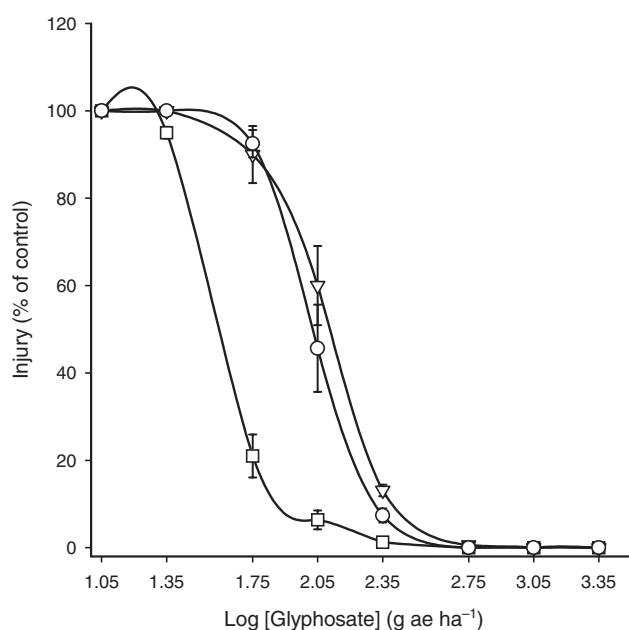


Fig. 1. Dose-response plots for the effects of Engame, Roundup Ultra and Touchdown formulations of glyphosate on prickly sida at 3 weeks after treatment. Data are the means \pm standard errors. Error bars smaller than the size of the symbol are not shown. 0, complete kill; 100, no injury. (∇), Roundup Ultra; (\square), Engame; (\circ), Touchdown.

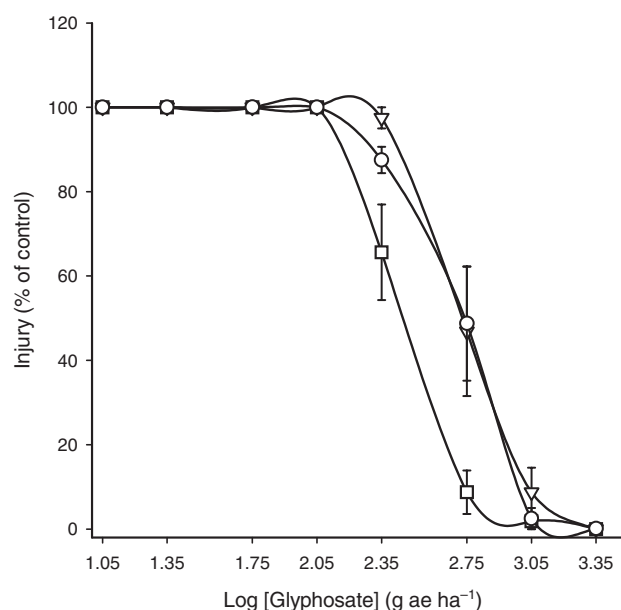


Fig. 2. Dose-response plots for the effects of Engame, Roundup Ultra and Touchdown formulations of glyphosate on purple nutsedge at 3 weeks after treatment. Data are the means \pm standard errors. Error bars smaller than the size of the symbol are not shown. 0, complete kill; 100, no injury. (∇), Roundup Ultra; (\square), Engame; (\circ), Touchdown.

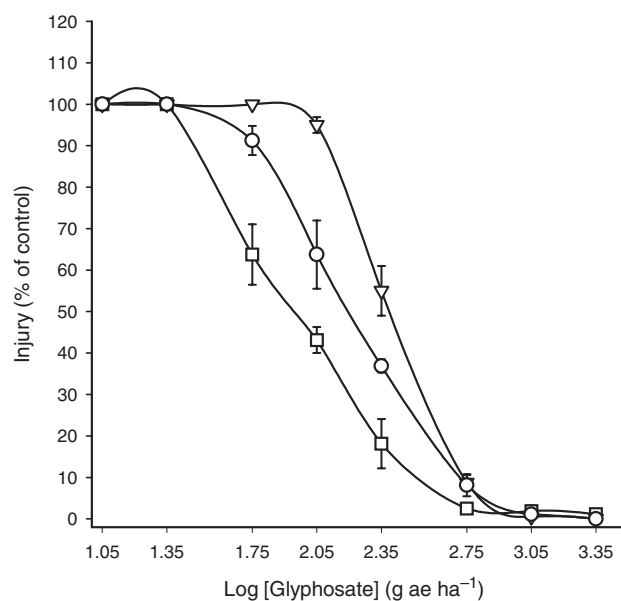


Fig. 3. Dose-response plots for the effects of Engame, Roundup Ultra and Touchdown formulations of glyphosate on morningglory at 3 weeks after treatment. Data are the means \pm standard errors. Error bars smaller than the size of the symbol are not shown. 0, complete kill; 100, no injury. (∇), Roundup Ultra; (\square), Engame; (\circ), Touchdown.

and the dose–response curves for these formulations were similar. Similar results have been observed with Roundup Ultra and Touchdown under field conditions (Mulkey *et al.* 1999). However, morningglory was more

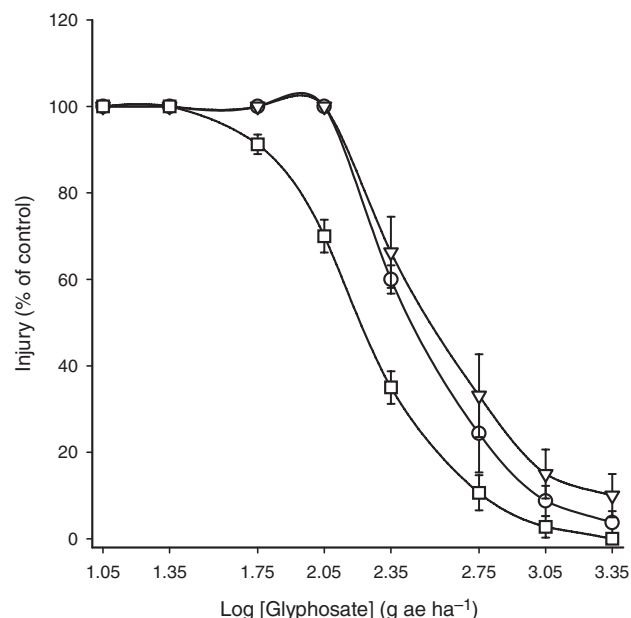


Fig. 4. Dose–response plots for the effects of Engame, Roundup Ultra and Touchdown formulations of glyphosate on sicklepod at 3 weeks after treatment. Data are the means \pm standard errors. Error bars smaller than the size of the symbol are not shown. 0, complete kill; 100, no injury. (▽), Roundup Ultra; (□), Engame; (○), Touchdown.

susceptible to Touchdown than to Roundup Ultra as indicated by the dose–response curves. At intermediate levels of control, the Engame formulation clearly differed from Touchdown and Roundup Ultra, which indicated that at doses that did not result in complete control, Engame was still the most active formulation. Laerka & Streibig (1995) used dose–response experiments to show that surfactants enhanced glyphosate acid activity and could lower the ED_{50} for glyphosate more than 20-fold.

The GR_{50} estimates for each glyphosate formulation were determined from the data in Figs 1–4 each week over a 3 week period because glyphosate produces its toxic effect more slowly than some other herbicides. For the weeds that were studied, the GR_{50} estimates for Engame were 2–3-fold lower than those determined for Roundup Ultra and Touchdown (Table 1), indicating that Engame was 2–3 times more active than the other formulations, as based on glyphosate acid equivalents. In addition, there was also no overlap in the asymptotic 95% confidence intervals between Engame and Roundup Ultra and Touchdown (Table 1), indicating that GR_{50} estimates were well-separated. Furthermore, GR_{50} estimates for each combination of weed and formulation across all dates were consistent with the relative ease or difficulty in controlling the weeds. The order of ease of control based on GR_{50} , prickly sida, morningglory, sicklepod and purple nutsedge, was maintained for each formulation. Indeed, if the maximum potential of glyphosate formulation was not achieved with Engame, then other new formulations might be found with even greater efficacy.

Table 1. Effect of glyphosate formulations on the GR_{50} estimates for four weed species

| Weed | Herbicide | GR_{50} glyphosate formulation (g ae ha ⁻¹) \pm SE [†] | | |
|-----------------|---------------|---|-------------------------|------------------------|
| | | 1 WAT | 2 WAT | 3 WAT |
| Morningglory | Roundup Ultra | 275 \pm 19 (236–314) | 173 \pm 9 (156–190) | 200 \pm 9 (182–218) |
| | Engame | 144 \pm 115 (121–167) | 58 \pm 5 (49–67) | 54 \pm 5 (44–64) |
| | Touchdown | 268 \pm 177 (233–303) | 112 \pm 6 (101–124) | 129 \pm 6 (117–142) |
| Prickly sida | Roundup Ultra | 122 \pm 9 (102–142) | 124 \pm 5 (114–135) | 112 \pm 4 (104–119) |
| | Engame | 38 \pm 3 (32–45) | 43 \pm 2 (40–47) | 40 \pm 2 (36–44) |
| | Touchdown | 103 \pm 7 (89–117) | 96 \pm 4 (89–104) | 86 \pm 3 (81–92) |
| Purple nutsedge | Roundup Ultra | 463 \pm 39 (386–541) | 434 \pm 23 (388–481) | 425 \pm 54 (316–533) |
| | Engame | 214 \pm 10 (194–233) | 196 \pm 13 (170–2210) | 217 \pm 14 (194–233) |
| | Touchdown | 452 \pm 41 (386–535) | 314 \pm 19 (276–353) | 576 \pm 59 (456–695) |
| Sicklepod | Roundup Ultra | 2546 \pm 1174 (225–4866) | 666 \pm 102 (464–868) | 370 \pm 19 (294–446) |
| | Engame | 1225 \pm 830 (414–2865) | 339 \pm 47 (246–432) | 173 \pm 19 (131–214) |
| | Touchdown | 1501 \pm 676 (165–2836) | 530 \pm 68 (395–665) | 302 \pm 19 (245–358) |

SE, standard error; WAT, weeks after treatment. [†] Asymptotic 95% confidence intervals in parentheses.

For prickly sida and purple nutsedge, the GR₅₀ estimates with asymptotic 95% confidence interval estimates for each formulation were similar at each evaluation time (Table 1). This consistency in GR₅₀ estimates with time can indicate that the sites of action of glyphosate had been sufficiently saturated as to cause immediate cessation of growth, so that there was little regrowth. However, for morningglory, the GR₅₀'s were higher at 1 WAT and then gradually decreased at 2 and 3 WAT, indicating either greater tolerance or slower response of morningglory to glyphosate in the glyphosate formulations (Table 1). Similar results were obtained for sicklepod. GR₅₀ estimates for sicklepod were highest at 1 WAT and decreased at 2 and then 3 WAT (Table 1), indicating that injury symptoms developed more slowly in sicklepod. GR₅₀ estimates for sicklepod were not different at 1 WAT among these formulations (Table 1), although over time Engame emerged as the most active formulation at 2 and 3 WAT.

For morningglory, GR₅₀ estimates for Touchdown were twice and the values for Roundup Ultra were three times that of Engame (Table 1). These results are consistent with the dose-response results in Fig. 3, which indicated three distinct curves. These differences in GR₅₀, especially between Roundup Ultra and Touchdown, might indicate that threshold concentrations of surfactants needed to increase glyphosate uptake were not considered for the species tested (Gaskin & Holloway 1992).

Prickly sida was more susceptible to Engame than the other formulations. There was rapid desiccation and necrosis development of the leaves within several hours of treatment. Similar effects were noted on morningglory, although its progression to complete control was slower for morningglory than for prickly sida. The initial injury might reflect cuticle thickness and injury can be due to the AMADS formulation rather than glyphosate itself. AMADS alone produced necrotic spots on leaf surfaces, but plants continued to grow without appreciable delay.

The increased activity of Engame probably reflects greater uptake and translocation to the sinks, which may result from increased tissue damage. Glyphosate absorption and translocation has been correlated with the dose (Kirkwood *et al.* 2000). Increased absorption and translocation of glyphosate was observed with the Engame formulation compared with Roundup Ultra (Westra *et al.* 2003). Engame was shown to cause severe cuticle disruption in the form of pits accompanied by tissue necrosis beneath the cuticle (Molin *et al.* 2003) and a direct

correlation between tissue necrosis and rapid rates of glyphosate uptake and translocation has been demonstrated (Feng *et al.* 1998). Considered together, these results might indicate that the surface injury noted with Engame may have facilitated the rapid uptake of glyphosate. However, the AMADS might have other effects on the plant systems that could contribute to enhanced glyphosate uptake and translocation. For example, AMADS may enhance glyphosate uptake by increasing retention on the plant surface. Nalewaja *et al.* (1995) showed that an increase in glyphosate injury could, in part, be affected by increased retention. AMADS might also affect translocation by providing foliar nutrients in the form of urea and sulfate. Further knowledge on the effects of the interaction between AMADS and glyphosate might lead to improvements in herbicide formulations.

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